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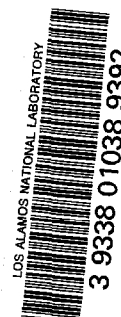
**CHEMICAL KINETICS OF THE AGING OF
ESTANE 5703 IN THE PLASTIC BONDED
EXPLOSIVE PBX 9501**

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Chemical Kinetics of the Aging of Estane 5703 in the Plastic Bonded Explosive PBX 9501

Russell T Pack and Michael R. Salazar

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ABSTRACT: This talk will review our progress in studying the chemical kinetics of the aging of Estane 5703 in PBX 9501. A brief motivation and review of earlier work will be given first. Then, progress made during the past year will be summarized, current conclusions will be given, and plans for future work will be given.



Chemical Kinetics of the Aging of Estane 5703 in PBX 9501



Russell T Pack and Michael R. Salazar

T-12, LANL

Energetic Materials Review

August 2001

ESC Task LA-24



The top half of each page is the slide that will be shown.
The lower half contains notes and comments that will be made.

This talk is to be given at the Energetic Materials Review at LANL, Aug 6-9,2001

We are studying the chemical kinetics of the aging of Estane 5703 in PBX 9501.



With Many Thanks to:

- Pat Foster, Paul Kramer, Erwin Kohn, Mike Lightfoot, Steve Malcolm, Tom Meyer, Wayne Rodin, Bobby Russell, Rusty Vincent, & Gail Watson, PX.
- Deanne Idar, Wayne King, Ken Laintz, Sheldon Larson, & Darla G. Thompson, DX-2, LANL
- Bruce Orler, Debra Wrobleski, & Jon Schoonover, MST-7, LANL
- Richard Browning, ESA-EA, LANL

This is a collaborative effort involving many people. These people are doing a great job and giving us a lot of help.

Motivation

- Estane[®] 5703 is used in PBX 9501 which is used extensively in the stockpile.
- The Estane is slowly degrading.
- The mechanical properties of the PBX depend on those of the Estane.
- Thus, safety and reliability issues require reliable prediction of those properties to long times.

This slide will be read without further comment.



Objectives

- Robust model of the chemical kinetics of Estane aging valid for all likely conditions to long times.
- Accurate connections of the chemical and mechanical properties.
- Reliable predictions of service lifetimes.

The accurate connections of the chemical and mechanical properties have not yet been made. When they are, then reliable predictions of the service lifetime of PBX 9501 under various conditions can be made.



Important Points

- Hydrolysis of the Estane is important and is becoming understood.
- Connections to mechanical properties are important. Not clear yet, but we see how to get them.
- Free radical reactions (crosslinking) are also important. Many unanswered questions remain.
- How we are addressing these issues.

This vugraph will simply be read to tell what the major points I plan to make are.

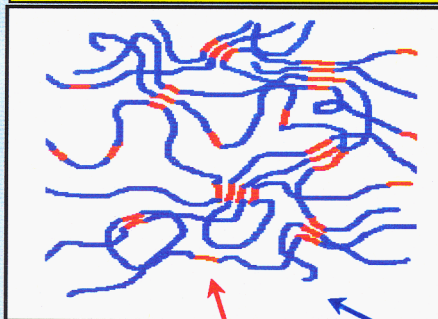


Composition of PBX 9501

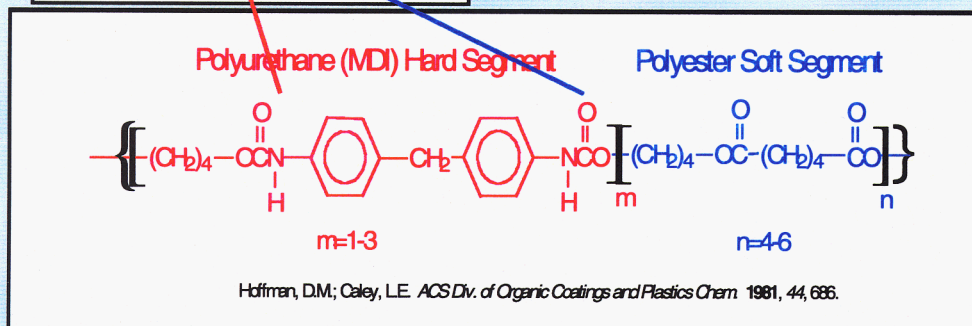
- 94.9% by wt. HMX (10 to 200 μ particles)
- 2.5% by wt. Estane 5703 (polymeric glue)
- 2.5% by wt. BDNPA/F nitroplasticizer (NP)
- 0.1% by wt. stabilizer. DPA or Irganox.

Will be read with little comment.

Estane 5703: Block copolymer



- Segmented poly(ester urethane)
- Phase separation of rigid aromatic hard segments and flexible soft segments



Well known facts about Estane. This slide will be used to note that hydrolysis attacks come at the ester links in the soft segment, and free radical attacks are thought to come at several points in the hard segments.



Which Mechanism Dominates?

- Free-radical oxidative degradation of urethane segments: Crosslinking, scission, radiolysis, or thermal degradation.
- Hydrolysis of the ester links in the soft segments.

We are almost half finished!



This vugraph will be read, and it will then be noted that one can make artificial aging conditions where any of several reactions dominate. The objective here is to determine which dominates in the mild conditions of storage in weapons. We now understand hydrolysis quite well but are just beginning to study free radical reaction reactions.

...

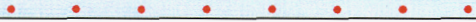
The LANL-PX collaboration has already established that:

- The "hump" in the MW was an artifact; the MW simply slowly declines in weapons storage.
 - Hydrolysis of ester links dominates the MW loss for aging in air at ambient humidities.
 - The Irganox is preventing runaway free-radical reactions in stockpile storage so far.
- ...

This vugraph will simply be read quickly to remind the audience of things that past work has established.



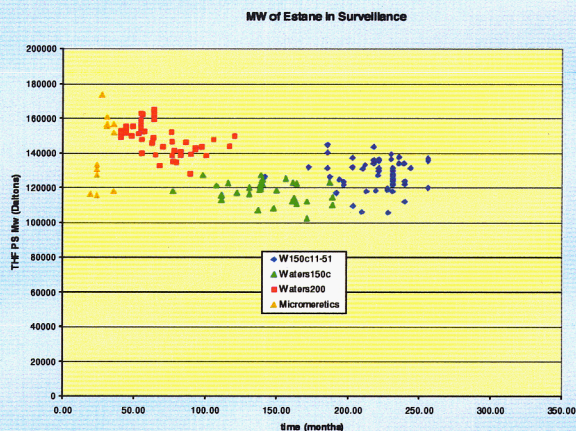
Error Bars for GPC Data

- Getting quantitative GPC data is difficult.
 - GPC is best evidence of aging inside weapons.
 - How much can GPC data restrict our models?
Used library and 622-7 data to determine.
 - Then, we obtained error bars on surveillance GPC data. Interesting implications.
 - See R. T Pack, LA-UR-01-2980 (June 2001) for details.
- 

GPC is gel permeation chromatography.

Surveillance Data

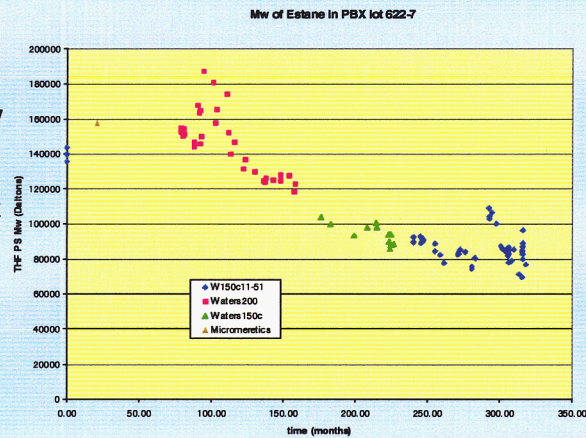
- A lot of scatter.
- Systematic differences between instruments.
- Any legitimate way to take out some scatter?
- Error bars?



From this vugraph, one sees that there is tremendous scatter in the GPC data from surveillance samples. Can we do anything to reduce that scatter or to put reasonable error bars on it? We use other data to determine the instrumental contribution to the scatter. Then the remainder will be real differences between samples.

Data on PBX 9501 lot 622-7.

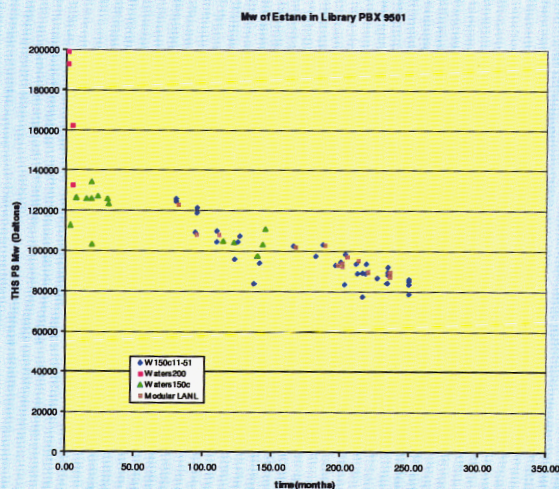
- Lot 622-7 PBX has been used as a standard for 27 years.
- Variations about a smooth curve are due to instruments.
- Note points for 3 new lots of Estane.



These are results on one old lot of PBX 9501, called 622-7, that has been stored in a magazine at PX for 27 years. It is used as a standard to check the instrument whenever any other samples are to be run. The one sure thing about this curve is that it should be smooth. Mostly read what is on slide.

Library PBX 9501 Data.

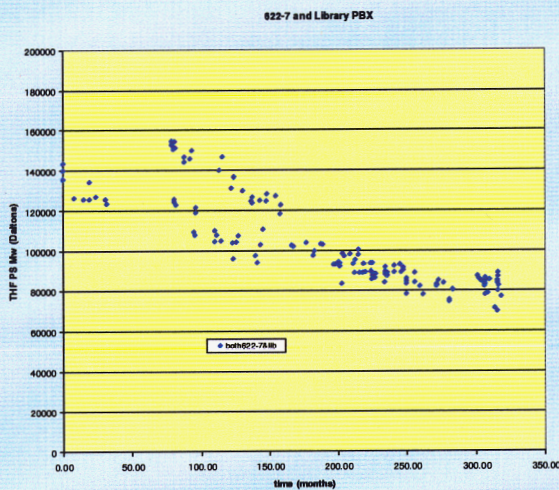
- Data from newer instruments fall on one curve.
- Waters 200 are systematically higher.
- Not lot to lot variation.
- Suggests scaling the W200 data by a $f=0.85$.
- Drop a few outliers.



Library samples of PBX 9501. Just read what is on vugraph.

Combined Library and 622-7.

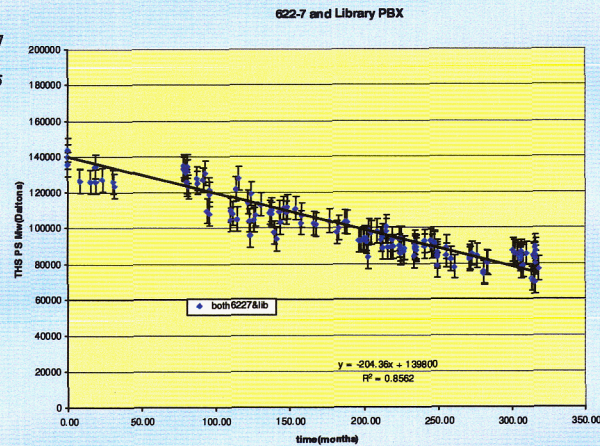
- Data from newer instruments fall on one curve.
- Waters 200 are systematically higher.
- Scale the W200 data to make average match W150.
- Do regression to optimize f.



Just read what is on vugraph.

Error Bars on 622-7 and Library.

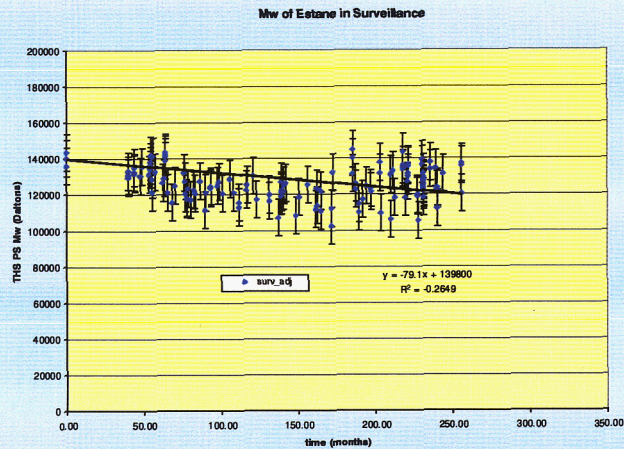
- Best $f=0.84$ but use compromise of 0.87
- Error bars are one σ (6700 D).
- On a given day, average σ is:
W200--3200,
W150c--2100,
W11-51--1100. So most is longer time variation.
- Now restricts any model much more.



Note that scale has now changed because variations are much smaller.

Error Bars on Surveillance Data.

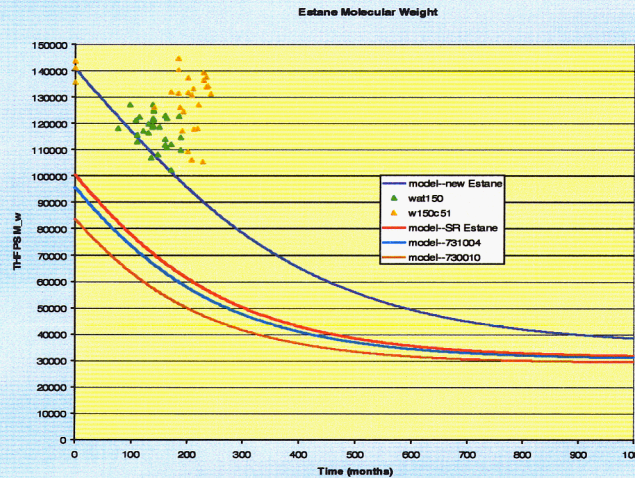
- Same procedure but outliers kept.
- Error bars are one $\sigma = 10200$ D.
- Scatter and size of later data unexplained.
- 99% should lie above 2.33σ below regression line.



This is now more restrictive than it was but still not totally understood. However, we do now have error bars.


Predicted Effect of Using Partially Degraded Estane.

- All calcs use same model.
- Worst case scenario for new Estane.
- Others begin with lower MW and more acid.
- $\tau_e = 50$ yr for new.
- $\tau_e = 25$ yr for SR
- $\tau_e = 23$ yr for 731-004.
- $\tau_e = 17$ yr for 730-010.




The upper line here is our best estimate of the behavior expected when PBX made with new Estane is stored in a W76. I showed it last year. Note that the leakage of the water out of the PBX cancels much of the autocatalytic behavior, so that this curve runs about half way between the curves on the preceding slide.

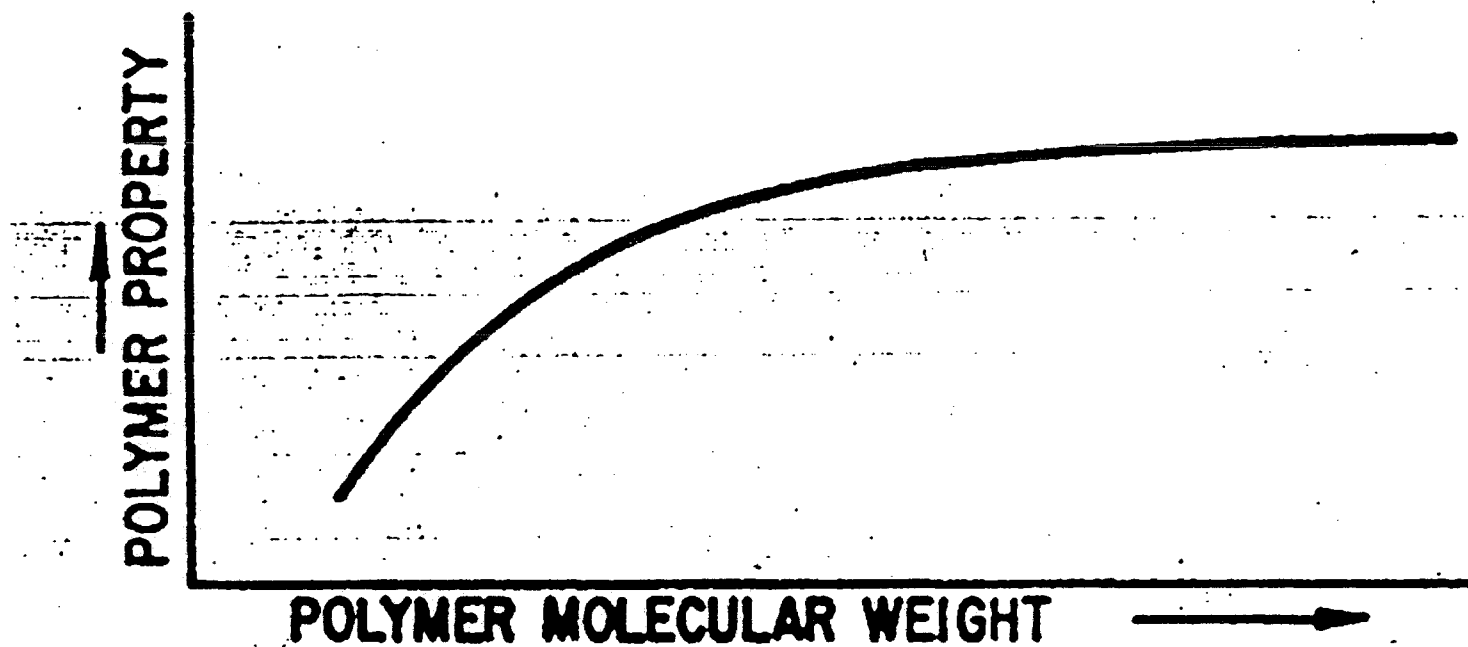
During this year, Deanne Idar, et al have been working to write new specifications on the Estane used to make PBX 9501 for weapons use. For that, I have made calculations assuming that the PBX used has either aged for a time or used Estane that has aged for a time before going into storage in a weapon. The same model is used as for the upper line. Because it makes a significant difference in the relaxation time of the molecular weight, we believe that MW standards for the Estane should be in the specifications.



Need: Mechanical Properties of Very Degraded PBX 9501

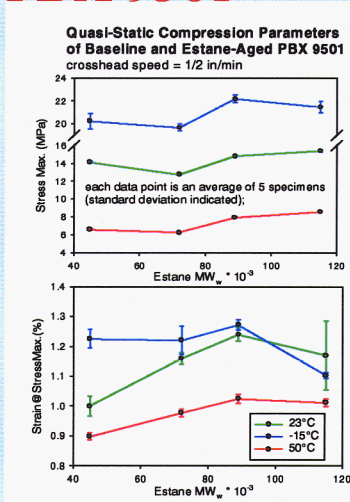
- Properties tend to an asymptote with MW.
 - Tensile strength of neat Estane shows this behavior. Orler.
 - Behavior is intensified by HMX filler.
 - Data to date shows little trend.
 - Still in asymptotic regime?
- 

This vugraph will simply be read.

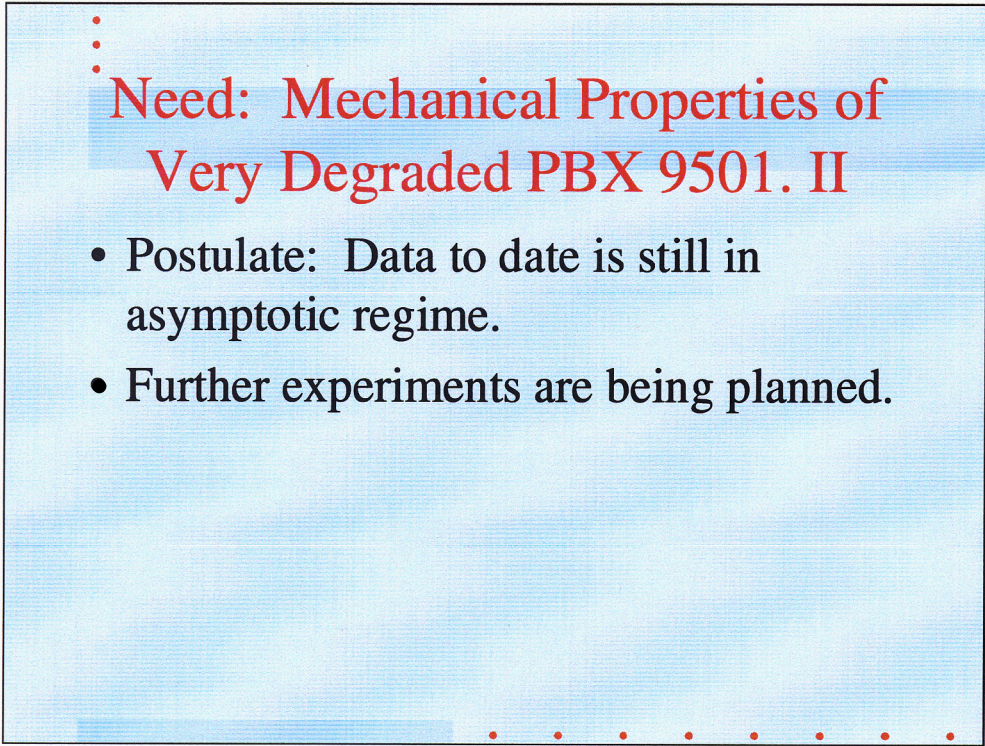


Compression Parameters of Virtually Aged PBX 9501

- Data of Darla G. Thompson. See her talk.
- No net trend of max. stress.
- Max. stress of neat HMX is about 4 MPa at room T. (Idar, et al, 1997).
- The strain at max. stress may be showing a trend, but it is still in the 1.1-1.3 % range for neat HMX. (Idar, et al, 1997).



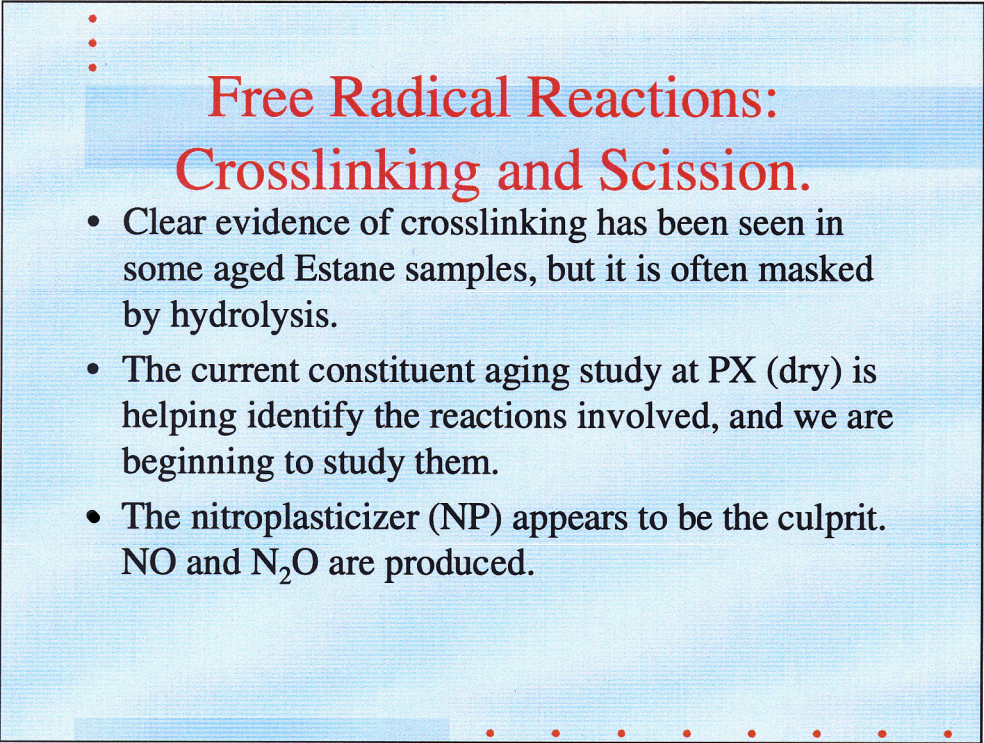
This will be used to illustrate the ideas on the previous slides



Need: Mechanical Properties of Very Degraded PBX 9501. II

- Postulate: Data to date is still in asymptotic regime.
- Further experiments are being planned.

This vugraph will simply be read.



Free Radical Reactions: Crosslinking and Scission.

- Clear evidence of crosslinking has been seen in some aged Estane samples, but it is often masked by hydrolysis.
- The current constituent aging study at PX (dry) is helping identify the reactions involved, and we are beginning to study them.
- The nitroplasticizer (NP) appears to be the culprit. NO and N₂O are produced.

Information about free radical reactions is beginning to come in and be studied. This vugraph will mostly be read. Much work remains to be done here.

Component Aging Study at PX

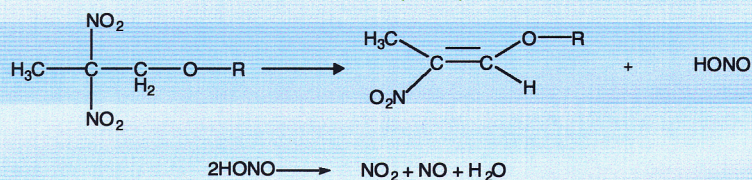
So far CAS experiments show:

- NP is largely responsible for gas evolution
- HMX is stable at experimental temperatures
- Estane is stable???
- Very interesting shift in gases and MWs when stabilized with DPA vs. Irganox

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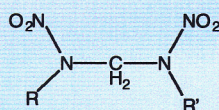
This shows what has been learned so far from the component aging study underway at PX.

Shaw, et al., Int. J. of Chem. Kinetics, V, 261 (1973).

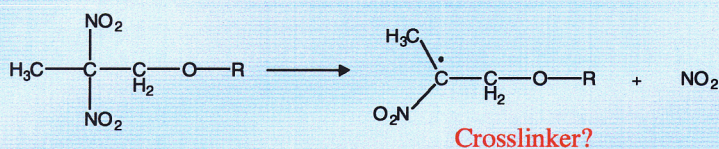


Brill, Prog. Energy Combust. Sci., 18, 91 (1992).

- from his large experience all N_2O emitters have



Kamlet, et al., Proceedings of the 7th Symposium on Detonations (1981).

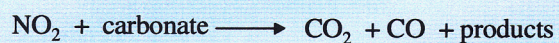
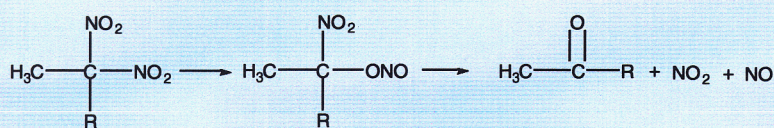
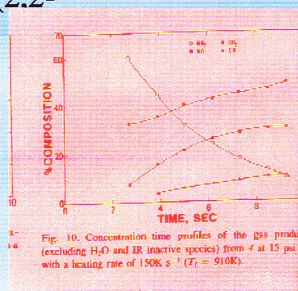
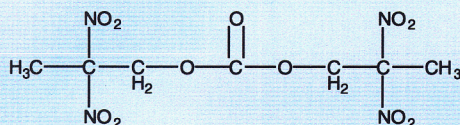


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Some possible free radical reactions of compounds similar to our nitroplasticizer.

- Brill, et al., *Combustion and Flame*, **65**, 103 (1986).

- studied the thermal decomposition of bis(2,2-dinitropropyl) carbonate



Theoretical Division - LANL

More free-radical reactions of compounds similar to NP.

A light blue rectangular box with a thin black border. In the top-left corner, there are three red dots arranged vertically. In the top-right corner, there are three red dots arranged horizontally. In the bottom-right corner, there are eight red dots arranged horizontally. The word "Conclusions" is centered in the box in a red serif font.

Conclusions

- Significant progress on many problems.
- Hydrolysis is becoming well understood.
- We see what is needed for the mechanical properties of aging PBX.
- Just beginning to study free-radical (crosslinking, etc.) reactions.
- Not finished and much remains to be done.
- We are getting there!

This vugraph will simply be read.